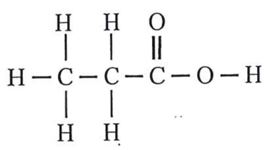
3. a. Combine excess acidified potassium permanganate solution and ethanol. [Ethanal may be substituted for ethanol.]
   b. React sodium metal [or $NaOH(aq)$] with ethanoic acid.
   c. Combine and reflux a mixture of methanol, ethanoic acid and a small amount of sulfuric acid (catalyst).
   d. React acidified potassium permanganate solution and 2-propanol.
   e. Pass propene gas through chlorine water.
   f. Combine and reflux a mixture of ethanol, butanoic acid and a small amount of sulfuric acid (catalyst).
   g. Treat 2-pentanol with excess acidified potassium permanganate solution .
   h. Combine methane gas and excess bromine gas. Expose the mixture to sunlight (UV radiation).
   i. Oxidise 1-propanol using limited acidified potassium dichromate solution. Keep the solution cold to minimise the formation of propanoic acid.

4. a. $nBrCH{=}CHBr \rightarrow -[CH(Br)-CH(Br)]_n-$
   b. $nClCH{=}CHCH_3 \rightarrow -[CH(Cl)CH(CH_3)]_n-$
   c. $nHO(CH_2)_7OH + nHOOC(CH_2)_2COOH \rightarrow -[O(CH_2)_7OOC(CH_2)_2CO]_n- + 2nH_2O$
   d. $nH_2N(CH_2)_5NH_2 + nHOOC(CH_2)_4COOH \rightarrow -[N(H)(CH_2)_5N(H)CO(CH_2)_4CO]_n- + 2nH_2O$

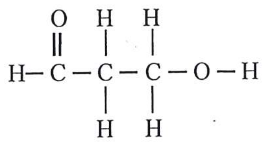
5. propanoic acid — The lack of reactivity with acidified potassium permanganate shows the compound is not an aldehyde, 1° or 2° alcohol. The reaction with sodium shows it contains a hydroxyl group (–OH). The substance could be a 3° alcohol or a carboxylic acid. Since a 3° alcohol is not possible with this molecular formula it must be a carboxylic acid.

6. A is



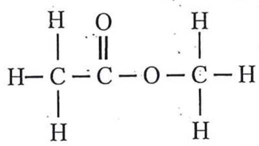
propanoic acid

B is



3-hydroxypropanal
Or 1-hydroxypropanone
Or 2-hydroxypropanal

C is



methyl ethanoate
Or ethyl methanoate

7. Add a single piece of sodium to each of **two** test tubes, say A and B.

   If either evolves a gas then that test tube contains **ethanol**. In this case add the drop of acidified potassium permanganate to test tube C. Discolouration identifies **butanal** and the remaining test tube contains **butanone**. If no discolouration occurs in test tube C then it contains **butanone** and the remaining test tube contains **butanal**.

   Alternatively, if neither A nor B liberates a gas then test tube C contains **ethanol**. In this case add the drop of acidified potassium permanganate to test tube A. Discolouration identifies **butanal** and test tube B contains **butanone**. If no discolouration occurs in test tube A then it contains **butanone** and test tube B contains **butanal**.

Unit 9 Set 21 Empirical formula

1. a. Since the compound contains only C, H and O and the sample has a mass of 3.433 g then:

$$m(O) = 3.433 - [m(C) + m(H)]$$
$$= 3.433 - (2.130 + 0.3575)$$
$$= 0.9455 \text{ g}$$

elements	C	H	O
mass of each	2.130 g	0.3575 g	0.9455 g
moles of each	0.1774	0.3547	0.05909
÷ by smallest ie by 0.05909 mol	$\frac{0.1774}{0.05909}$	$\frac{0.3547}{0.05909}$	$\frac{0.05909}{0.05909}$
ratio	3.00	6.00	1.00
empirical formula	$\mathbf{C_3H_6O}$		

Answers

b. $PV = nRT$ *ie* $n = \frac{PV}{RT} = \frac{80.2 \times 2.25}{8.3145 \times 408} = 0.0532$ mol

Find the moles of gas using the ideal gas law. Take care to use the correct value of R. Temperature in kelvin.

$n = \frac{m}{M}$ *ie* $M = \frac{m}{n} = \frac{6.182}{0.0532} = 116$ g mol^{-1}

Find the molar mass of the compound.

$M(C_3H_6O) = 3 \times 12.01 + 6 \times 1.008 + 16.00 = 58.08$ g mol^{-1}

Determine the empirical formula mass from the empirical formula, ie C_3H_6O.

$\text{ratio} = \frac{\text{molecular formula mass}}{\text{empirical formula mass}} = \frac{116}{58.08} = 2.00$

This shows the molecular formula is twice the empirical formula.

∴ molecular formula $= \mathbf{C_6H_{12}O_2}$

c. **ethyl butanoate**

a. Since the sum of the two percentages is 100, then: %H = 100 - %C = 100 - 85.66 = 14.34 %

elements	C	H
% of each	85.66 %	14.34 %
mass in a 100 g	85.66g	14.34g
moles in 100 g	$\frac{85.66}{12.01}$	$\frac{14.34}{1.008}$
	7.132	14.23
÷ by smallest	$\frac{7.132}{7.132}$	$\frac{14.23}{7.132}$
ratio	1.00	1.995

∴ the empirical formula is CH_2

b. $n = \frac{V(STP)}{22.4} = \frac{1.00}{22.4} = 0.0446$ mol *and* $n = \frac{m}{M}$ *ie* $M = \frac{m}{n} = \frac{1.88}{0.0446} = 42.1$ g mol^{-1}

$M(CH_2) = 12.01 + 2 \times 1.008 = 14.03$ g mol^{-1}

$\text{ratio} = \frac{\text{molecular formula mass}}{\text{empirical formula mass}} = \frac{42.1}{14.03} = 3.00$

This shows the molecular formula is three times the empirical formula.

∴ molecular formula = C_3H_6

c. **propene**

The presence of a double bond is confirmed by the rapid reaction with bromine water.

a. $n(CO_2) = \frac{m}{M} = \frac{12.16}{44.01} = 0.2763$ mol

$n(C) = n(CO_2) = 0.2763$ mol

Since there is one mole of C in every mole of CO_2.

$m(C) = n \times M = 0.2763 \times 12.01 = 3.318$ g

$n(H_2O) = \frac{m}{M} = \frac{4.563}{18.016} = 0.2533$ mol

$n(H) = 2 \times n(H_2O) = 2 \times 0.2533 = 0.5065$ mol

As there are two moles of H in every mole of H_2O.

$m(H) = n \times M = 0.5065 \times 1.008 = 0.5106$ g

$m(O) = 7.882 - [m(C) + m(H)] = 7.882 - (3.318 + 0.5106) = 4.053$ g

The sample contains C, H and O only.

C	H	O
3.318g	0.5106 g	4.053 g
$\frac{3.318}{12.01}$	$\frac{0.5106}{1.008}$	$\frac{4.053}{16.00}$
0.2763	0.5065	0.2533
1.091	2.00	1.000
12.00	22.00	11.00

Find the moles of each element, ie divide the mass of each element by its molar mass.

Divide all by the smallest molar value, ie 0.2533.

Multiplying by 11 produces a whole number ratio.

∴ the empirical formula is $C_{12}H_{22}O_{11}$

b. $PV = nRT$ *ie* $n = \frac{PV}{RT} = \frac{101.9 \times 0.3242}{8.3145 \times 438} = 9.071 \times 10^{-3}$ mol

Take care to use the correct value of R. Temperature in kelvin, volume in litres.

and $M(\text{molecular}) = \frac{m}{n} = \frac{3.115}{9.071 \times 10^{-3}} = 343.4$ g mol^{-1} *also* $M(\text{Empirical}) = 12 \times 12.01 + 22 \times 1.008 + 11 \times 16.00 = 342.30$ g mol^{-1}

$\text{ratio} = \frac{\text{molecular formula mass}}{\text{empirical formula mass}} = \frac{343.4}{342.30} = 1.003$

This shows the molecular formula is the same as the empirical formula.

∴ molecular formula = $C_{12}H_{22}O_{11}$

4. a. $n(H_2O) = \frac{m}{M} = \frac{8.198}{18.016} = 0.4550$ mol

$n(H) = 2 \times n(H_2O) = 2 \times 0.4550 = 0.9101$ mol

As there are two moles of H in every mole of H_2O.

$m(H) = n \times M = 0.9101 \times 1.008 = 0.9174$ g

$m(C) = 5.249 - m(H) = 5.249 - 0.9174 = 4.332$ g

As the sample contains the elements C and H only.

C	H	
4.332 g	0.9174 g	
$\frac{4.332}{12.01}$	$\frac{0.9174}{1.008}$	Find the moles of each element, ie divide the mass of each element by its molar mass.
0.3607	0.9101	Divide all by the smallest molar value, ie 0.3607.
1.000	2.523	Multiplying by 2 produces a whole number ratio.
2.000	5.047	

∴ the empirical formula is C_2H_5

b. $PV = nRT$ *ie* $n = \frac{PV}{RT} = \frac{102.5 \times 1.289}{8.3145 \times 296.5} = 0.05359$ mol

Take care to use the correct value of R. Temperature in kelvin.

and $M(\text{molecular}) = \frac{m}{n} = \frac{3.121}{0.05359} = 58.23 \text{ g mol}^{-1}$ *also* $M(C_2H_5) = 2 \times 12.01 + 5 \times 1.008 = 29.06 \text{ g mol}^{-1}$

$\text{ratio} = \frac{\text{molecular formula mass}}{\text{empirical formula mass}} = \frac{58.23}{29.06} = 2.004$

This shows the molecular formula is twice the empirical formula.

∴ molecular formula = C_4H_{10}

5. a. $n(CO_2) = \frac{m}{M} = \frac{7.974}{44.01} = 0.1812$ mol

$n(C) = n(CO_2) = 0.1812$ mol

Since there is one mole of C in every mole of CO_2.

$m(C) = n \times M = 0.1812 \times 12.01 = 2.176$ g

$n(H_2O) = \frac{m}{M} = \frac{3.264}{18.016} = 0.1812$ mol

$n(H) = 2 \times n(H_2O) = 2 \times 0.1812 = 0.3623$ mol

As there are two moles of H in every mole of H_2O.

$m(H) = n \times M = 0.3623 \times 1.008 = 0.3652$ g

$m(O) = 3.996 - [m(C) + m(H)] = 3.991 - (2.176 + 0.3652) = 1.455$ g

As the sample contains C, H and O only.

C	H	O	
2.176 g	0.3652 g	1.455 g	
$\frac{2.176}{12.01}$	$\frac{0.3652}{1.008}$	$\frac{1.455}{16.00}$	Find the moles of each element, ie divide the mass of each element by its molar mass.
0.1812	0.3623	0.09092	Divide all by the smallest molar value, ie 0.09092.
1.993	3.985	1.000	

∴ the empirical formula is C_2H_4O

b. $PV = nRT$ *ie* $n = \frac{PV}{RT} = \frac{125.4 \times 0.4468}{8.3145 \times 458.5} = 0.01470$ mol

Take care to use the correct value of R. Temperature in kelvin.

and $M(\text{molecular}) = \frac{m}{n} = \frac{1.289}{0.01470} = 87.70 \text{ g mol}^{-1}$ *also* $M(C_2H_4O) = 2 \times 12.01 + 4 \times 1.008 + 16.00 = 44.05 \text{ g mol}^{-1}$

$\text{ratio} = \frac{\text{molecular formula mass}}{\text{empirical formula mass}} = \frac{87.70}{44.05} = 1.991$

This shows the molecular formula is twice the empirical formula.

∴ molecular formula = **$C_4H_8O_2$**

c. **butanoic acid or 2-methylpropanoic acid**

An -OH group is indicated by the reaction with sodium. The lack of reactivity with acidified $KMnO_4$ indicates the compound is not a 1° alcohol, 2° alcohol or aldehyde.

6. a. $n(CO_2) = \dfrac{m}{M} = \dfrac{3.219}{44.01} = 0.07314$ mol $n(C) = n(CO_2) = 0.07314$ mol Since there is one mole of C in every mole of CO_2.

$m(C) = n \times M = 0.07314 \times 12.01 = 0.8784$ g

$n(H_2O) = \dfrac{m}{M} = \dfrac{1.537}{18.016} = 0.08531$ mol $n(H) = 2 \times n(H_2O) = 2 \times 0.08531 = 0.1706$ mol As there are two moles of H in every mole of H_2O.

$m(H) = n \times M = 0.1706 \times 1.008 = 0.1720$ g

$n(N_2) = \dfrac{PV}{RT} = \dfrac{102.1 \times 0.3003}{8.3145 \times 302.5} = 0.01219$ mol The combustion of alanine released 300.3 mL of nitrogen at 102.1 kPa and 302.5 K.

$m(N) = m(N_2) = n\,M = 0.01219 \times 28.02 = 0.3416$ g Nitrogen is collected as N_2 thus its molar mass is 28.02 g mol^{-1}.

$m(O) = 2.170 - [m(C) + m(H) + m(N)]$

$= 2.170 - (0.07314 + 0.1720 + 0.3416) = 0.7780$ g

The sample contains the elements C, H, N and O only.

C	H	N	O	
0.8784 g	0.1720 g	0.3416 g	0.7780 g	
$\dfrac{0.8784}{12.01}$	$\dfrac{0.1720}{1.008}$	$\dfrac{0.3416}{14.01}$	$\dfrac{0.7780}{16.00}$	Find the moles of each element, ie divide the mass of each element by its molar mass.
0.07314	0.1706	0.02438	0.04862	Divide all by the smallest molar value, ie 0.02438.
3.000	6.998	1.000	1.994	

∴ the empirical formula is $\mathbf{C_3H_7NO_2}$

b. $M(C_3H_7NO_2) = 3 \times 12.01 + 7 \times 1.008 + 14.01 + 2 \times 16.00$
$= 89.10$ g mol^{-1}

ratio $= \dfrac{\text{molecular formula mass}}{\text{empirical formula mass}} = \dfrac{88.7}{89.10} = 0.996$

∴ molecular formula $= \mathbf{C_3H_7NO_2}$ This shows the molecular formula is the same as the empirical formula.

c.

```
        NH2
        |
    CH3CHC — OH
          ||
          O
```

7. a. $n(CO_2) = \dfrac{m}{M} = \dfrac{10.60}{44.01} = 0.2409$ mol $n(C) = n(CO_2) = 0.2409$ mol Since there is one mole of C in every mole of CO_2.

$m(C) = n \times M = 0.2409 \times 12.01 = 2.893$ g

$n(H_2O) = \dfrac{m}{M} = \dfrac{2.136}{18.016} = 0.1186$ mol $n(H) = 2 \times n(H_2O) = 2 \times 0.1186 = 0.2371$ mol As there are two moles of H in every mole of H_2O.

$m(H) = n \times M = 0.2371 \times 1.008 = 0.2390$ g

$m(O) = 10.79 - [m(C) + m(H)] = 10.79 - (2.893 + 0.2390) = 7.658$ g The sample contains C, H and O only.

C	H	O	
2.893 g	0.2390 g	7.658 g	
$\dfrac{2.893}{12.01}$	$\dfrac{0.2390}{1.008}$	$\dfrac{7.658}{16.00}$	Find the moles of each element, ie divide the mass of each element by its molar mass.
0.2409	0.2371	0.4786	Divide all by the smallest molar value, ie 0.2371.
1.016	1.000	2.019	

∴ the empirical formula is $\mathbf{CHO_2}$

b. $n(NaOH) = c\,V = 0.2021 \times 16.25 \times 10^{-3} = 3.284 \times 10^{-3}$ mol

$n(\text{acid in 20 mL}) = \dfrac{1}{2}\, n(NaOH) = \dfrac{1 \times 3.284 \times 10^{-3}}{2} = 1.642 \times 10^{-3}$ mol The compound is a diprotic acid ∴ contains two carboxylic acid groups per molecule, ie

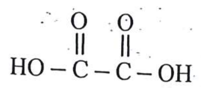
$n(\text{acid in 250 mL}) = \dfrac{250}{20} \times 1.642 \times 10^{-3} = 2.053 \times 10^{-2}$ mol $2NaOH + H_2X \rightarrow Na_2X + 2H_2O$

and $M(\text{acid}) = \dfrac{m}{n} = \dfrac{1.851}{2.053 \times 10^{-2}} = 90.18$ g mol^{-1} *also* $M(CHO_2) = 12.01 + 1.008 + 2 \times 16.00$
$= 45.02$ g mol^{-1}

ratio $= \dfrac{\text{molecular formula mass}}{\text{empirical formula mass}} = \dfrac{90.18}{45.02} = 2.003$

∴ molecular formula $= \mathbf{C_2H_2O_4}$

c.



8. a. $n(CaCO_3) = \frac{m}{M} = \frac{31.34}{100.09} = 0.3131$ mol

$n(C) = n(CaCO_3) = 0.3131$ mol

There is one mole of carbon in each mole of $CaCO_3$.

$m(C) = n \times M = 0.3131 \times 12.01 = 3.761$ g

$m(H) = 4.413 - m(C) = 4.413 - 3.761 = 0.6525$ g

As the sample contains C and H only.

C	H	
3.761 g	0.6525	
$\frac{3.761}{12.01}$	$\frac{0.6525}{1.008}$	
0.3131	0.6473	
1.000	2.067	Divide all by the smallest molar value, ie 0.3131.

∴ the empirical formula is CH_2

b. $n = \frac{PV}{RT} = \frac{129.5 \times 1.754}{8.3145 \times 349} = 0.07828$ mol

and $M(\text{molecular}) = \frac{m}{n} = \frac{4.485}{0.7828} = 57.30$ g mol^{-1}

$M(CH_2) = 12.01 + 2 \times 1.008$
$= 14.03$ g mol^{-1}

$\text{ratio} = \frac{\text{molecular formula mass}}{\text{empirical formula mass}} = \frac{57.30}{14.03} = 4.085$

∴ molecular formula = C_4H_8

c. **cyclobutane** or **methylcyclopropane**

The slow reaction with bromine excludes the presence of a double bond.

9. *This analysis involves two separate samples (a 1.279 g sample and a 1.625 g sample). In situations like this it is convenient to determine the percentage composition of the individual elements within each sample. The percentage composition of the compound can then be used to find the empirical formula.*

Determine the %C and %H in the 1.279 g sample.

$n(CO_2) = \frac{m}{M} = \frac{1.600}{44.01} = 0.03636$ mol

$n(C) = n(CO_2) = 0.03636$ mol

Since there is one mole of C in every mole of CO_2.

$m(C) = n \times M = 0.03636 \times 12.01 = 0.4366$ g *and* $\%(C) = \frac{m(C)}{m(\text{sample})} \times 100 = \frac{0.4366 \times 100}{1.279} = 34.14$ %C

$n(H_2O) = \frac{m}{M} = \frac{0.7700}{18.016} = 0.04274$ mol

$n(H) = 2 \times n(H_2O) = 2 \times 0.04274 = 0.08548$ mol

As there are two moles of H in every mole of H_2O.

$m(H) = n \times M = 0.08548 \times 1.008 = 0.08616$ g *and* $\%(H) = \frac{m(H)}{m(\text{sample})} \times 100 = \frac{0.08616 \times 100}{1.279} = 6.737$ %H

Determine the %N in the 1.625 g sample.

$n(N_2) = \frac{PV}{RT} = \frac{102.5 \times 0.1830}{8.3145 \times 293.0} = 7.700 \times 10^{-3}$ mol

Decomposition of the sample released 183.0 mL of nitrogen gas (N_2) at 102.5 kPa and 293.0 K.

$m(N) = m(N_2) = n\,M$
$= 7.700 \times 10^{-3} \times 28.02 = 0.2157$ g of N *and* $\%(N) = \frac{m(N)}{m(\text{sample})} \times 100 = \frac{0.2157 \times 100}{1.625} = 13.28$ %N

Determine the %O in the compound by subtraction.

$\%(O) = 100.0 - [\%C + \%H + \%N] = 100.0 - (34.14 + 6.737 + 13.28) = 45.85$ % O

Determine the empirical formula from the percentage composition of the compound.

C	H	O	N	
34.14 %	6.737 %	45.85 %	13.28 %	The % by mass of each element in the compound.
34.14 g	6.737 g	45.85 g	13.28 g	The mass of each element in 100.0 g of compound.
$\frac{34.14}{12.01}$	$\frac{6.737}{1.008}$	$\frac{45.85}{16.00}$	$\frac{13.28}{14.01}$	Find the moles of each element, ie divide the mass of each element by its molar mass.
2.842	6.683	2.866	0.9476	Divide all by the smallest molar value, ie 0.9476.
3.000	7.053	3.024	1.000	

∴ the empirical formula is $C_3H_7O_3N$

02 *Answers*

0. *Determine the %C and %H in the 7.335 g sample.*

$n(CO_2) = \frac{m}{M} = \frac{15.36}{44.01} = 0.3490$ mol $\quad n(C) = n(CO_2) = 0.3490$ mol $\quad$ Since there is one mole of C in every mole of CO_2.

$m(C) = n \times M = 0.3490 \times 12.01 = 4.192$ g $\quad$ *and* $\quad \%(C) = \frac{m(C)}{m(aspartame)} \times 100 = \frac{4.192 \times 100}{7.335} = 57.15\ \%C$

$n(H_2O) = \frac{m}{M} = \frac{4.041}{18.016} = 0.2243$ mol $\quad n(H) = 2 \times n(H_2O) = 2 \times 0.2243 = 0.4486$ mol

As there are two moles of H in every mole of H_2O.

$m(H) = n \times M = 0.4486 \times 1.008 = 0.4522$ g $\quad$ *and* $\quad \%(H) = \frac{m(H)}{m(aspartame)} \times 100 = \frac{0.4552 \times 100}{7.335} = 6.165\ \%H$

Use the titration data to determine the amount of NH_3 and thus % N present in the second 4.719 g aspartame sample.

$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

$n(NaOH) = c\,V = 0.1249 \times 28.18 \times 10^{-3} = 3.520 \times 10^{-3}$ mol $\quad$ *and* $\quad$ n(HCl remaining in 100 mL) = n(NaOH) = 3.520×10^{-3} mol

n(HCl originally in the 100 mL solution) = $c\,V = 0.3559 \times 0.1000 = 3.559 \times 10^{-2}$ mol HCl

$n(NH_3$ reacting with HCl) = n(HCl originally present in 100 mL) - n(HCl remaining in 100 mL)

$= 3.559 \times 10^{-2} - 3.520 \times 10^{-3} = 3.207 \times 10^{-2}$ mol NH_3

$n(N) = n(NH_3) = 3.207 \times 10^{-2}$ mol $\quad$ *and* $\quad m(N) = n\,M = 3.207 \times 10^{-2} \times 14.01 = 0.4493$ g

$\%(N) = \frac{m(N)}{m(aspartame)} \times 100 = \frac{0.4493 \times 100}{4.719} = 9.521\ \%N$

Determine the %O in the compound by subtraction.

$\%(O) = 100.0 - [\%C + \%H + \%N] = 100.0 - (57.15 + 6.165 + 9.521) = 27.17\ \%\ O$

Determine the empirical formula from the percentage composition of the compound.

C	H	O	N	
57.15 %	6.165 %	27.17 %	9.521 %	The % by mass of each element in aspartame.
57.15 g	6.165 g	27.17 g	9.521 g	The mass of each element in 100.0 g of aspartame.
$\frac{57.15}{12.01}$	$\frac{6.165}{1.008}$	$\frac{27.17}{16.00}$	$\frac{9.521}{14.01}$	Find the moles of each element, ie divide the mass of each element by its molar mass.
4.758	6.116	1.698	0.6796	Divide all by the smallest molar value, ie 0.6796.
7.001	9.000	2.499	1.000	Multiply all values by 2 for a whole number ratio.
14.02	18.00	4.997	2.000	Multiply all values by 2 for a whole number ratio.

∴ the empirical formula is $C_{14}H_{18}N_2O_5$